Supporting Information

London dispersion corrections to density functional theory for transition-metals based on fitting to experimental temperature-programmed desorption of benzene monolayers

*Hao Yang[a], Tao Cheng[a,] * and William A. Goddard III[b,] **

[a]Institute of Functional Nano and Soft Materials (FUNSOM), Soochow University, Suzhou 215123, China

[b]Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125, USA

Content

1. Computational details

The density functional theory (DFT) calculations are performed by using Vienna Ab initio Simulation Package (VASP) at a version of 5.4.4 [1, 2] with the projector augmented wave (PAW) method and a plane wave basis set. The method is density functional theory (DFT) with generalized gradient approximations (GGA) of Perdew-Burke-Ernzerhof (PBE) functional[3] The energy cut-off is set to 600 eV. The convergence criteria were 1.0×10^{-6} eV for energy and 1.0×10^{-4} eV/Å for forces. Collinear spin polarized calculations are included.

For calculations of the cohesive energy we used the $d^{10}s^1$ state of Cu, Ag, Au, the d^{10} state of Pd, and the d^9s^1 state of Pt. The ground state of Ni atom is the ^3F $(3d^8)(4s)^2$ state, but for Ni atom VASP assumes that there are 8/5 electrons in each of the five d orbitals, which leads to an energy that is 30% ^3P and 70% ^3F. Thus, we corrected the VASP Ni atom energy by making it 0.535 eV = 51.65 kJ/mol more stable.

The vdW corrections are considered either in Grimme-Becke-Johnson empirical D3 model,[4, 5]

$$E_{disp} = -\frac{1}{2}\sum_{i=1}^{Nai}\sum_{k=1}^{Nai}\sum_{L}{}'\left(f_{d,6}(r_{ik,L})\frac{C_{6ik}}{r_{ik,L}^{6}} + f_{d,8}(r_{ik,L})\frac{C_{8ik}}{r_{ik,L}^{8}} \right) \qquad \text{(S1)}$$

where $f_{d,n}(r_{ik}) = \dfrac{s_n r_{ik}^n}{r_{ik}^n + (a_1 R_{0ik} + a_2)^n}$,

or in the LG form[6, 7]

$$\mathrm{E}_{ik-dispersion} = -\sum_{ik,i<k}^{\mathrm{N}} \frac{C_{6LG\text{-}ik}}{R_{0ik}^6 + R_{vdwLG\text{-}ik}{}^6} \qquad \text{(S2)}$$

where $C_{6LG\text{-}ik}$ and $R_{vdwLG\text{-}ik}$ are optimized to fit binding of physisorbed molecules for atoms i and k and R_{ik} is the variable distance between atoms i and k. Note here that

the paper by Hyunjun *et. al*. [7]reporting LG parameters for all elements up to Z=103 (Lr) used the convention that R_{vdw} is half the vdw minimum. We now use the full vdw distance.

We assume geometric mean combination rules so that

$$C_{6LG-ik} = \sqrt{C_{6LG-ii} \times C_{6LG-kk}} \quad \text{(S3a)}$$

$$R_{vdwLG-ik} = \sqrt{R_{vdwLG-ii} \times R_{vdwLG-kk}} \quad \text{(S3b)}$$

Thus at $R_{0ik} = R_{vdwLG-ik}$, we have $E_{ik\text{-dispersion}} = - ½ C_6/(R_{0ik})^6$.

With the LG form (S2), $E_{ij\text{-dispersion}}$ is nearly constant for $R<<R_0$ with a small value of $E_{ik\text{-dispersion}} = - C_6/(R_{0ik})^6$. Thus this LG correction has very little impact on the valence interactions already described well by the PBE functional. Some proposed dispersion corrections are adjusted to be zero for normal bond distances.[8] We do not do this because we want the dispersion correction to be monotonically attractive while remaining small.

Our implementation of the LG correction for use in VASP uses a python interface that is included in the SI. The low-gradient parameters for carbon (C) and hydrogen (H) are directly from the previously published paper with no additional fitting (but changing the convention on R_{vdw}).[7]

2. Estimation of reaction enthalpy of benzene and other adsorbed species on metal surface using quantum mechanics methods

To match the experimental reaction enthalpy, we calculated the Gibbs free energies of each species on the metal surface at the experimental temperature according to the published data.[9] The calculated Gibbs free energies is given by

$$G = E_{PBE} + E_{vdW} + E_{ZPE} + \int C_p T \quad \text{(S4)}$$

Where the E_{PBE} is the electronic energy, and the E_{vdW} is the long-range dispersion correction term. The last two terms in S4 are the zero-point energy and the temperature corrected enthalpy at the experimental temperature.

The detailed computational process for Gibbs free energy is as follows: firstly, the adsorbed geometries are optimized using pure PBE, PBE-D3(BJ) and PBE-LG (using the newly fitted low gradient parameters). Secondly, the thermal correction were performed for the various equilibrium configurations, using density functional perturbation theory (DFPT) to calculate the phonon density of states at the specified temperature (experimental temperature). All vibrational frequencies for surface adsorbents are calculated by allowing the adsorbed molecules and the top layer of metal to relax, but with the bottom layers fixed.

The Nelder-Mead method as implemented in SciPy was employed to cost the following cost function (E_{error}):

$$E_{error} = \sum_{i=0}^{N} \frac{1}{w_i^2} \left(E_{PBE-LG} - E_{Exp.}\right)^2 \quad \text{(S5)}$$

Here, N is the total number of training set. w_i is the weight for each data point in the training set. $E_{PBE\text{-}LG}$ is the binding energy from PBE-LG, $E_{Exp.}$ is the binding energy from experiment.

In the training, all the w_i were set to 1. In $E_{\mathrm{PBE\text{-}LG}}$, both zero-point energy (E_{ZPE}) correction and phonon correction (E_{phon}) are included. The initial LG parameters were taken from our previous paper,[7] and further optimized to minimize E_{error}.

3. Fitting the new LG parameters for selected transition metals

For Pt, Cu, Ag and Au crystals, we obtained new LG parameters (C_6&R_{vdW}) by calculating the equation of states (EoS) and matching to the experimental cohesive energy at the experimental volume (obtained by extrapolation to 0 K). We consider that the optimized geometries from PBE-D3 method may be reliable, so we adjust only the binding enthalpy to fit experiment.

For Ni and Pd the calculated cohesive energy using pure PBE is already overestimated, here we allow the C_6 LG parameter to be negative.

4. Implementation of LG input for VASP

We have written a code, LG-VASP, based on the Atomic Simulation Environment (ASE),[8] to convert the LG input parameters, C_6 and R_{vdw}, into the form required by VASP. This uses the geometric mean cross terms for all pairs of elements. LG-VASP uses the same functional as currently implemented in VASP, but with the input parameters are adjusted to the LG form. This code is attached.

The LG-VASP code can also extract the energy and force from the VASP output. The LG correction is calculated based on the same geometry. After correction, the total energy is

$$E_{total} = E_{QM} + E_{LG} \quad \text{(S6)}$$

and the total force is

$$F_{total} = F_{QM} + F_{LG} \quad \text{(S7)}$$

The total energy and total force can be used in optimization methods as implemented in ASE, such as BFGS, LBFGS, etc. In principle, this code can be easily coupled with other Quantum Mechanics Code, such as Quantum Espresso, CP2K, etc.

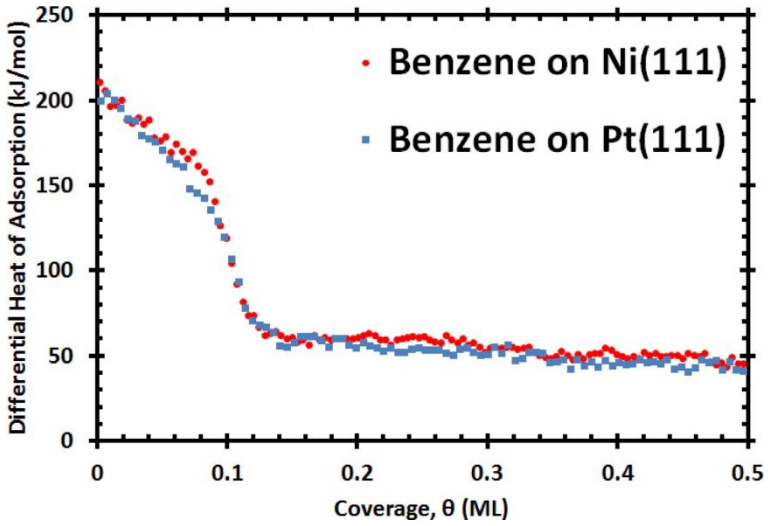

Figure S1. Experimental measurement of the differential heat of adsorption of benzene on Ni(111) and Pt(111) under different adsorbed benzene coverage. Copyright: Elsevier 2018.[9]

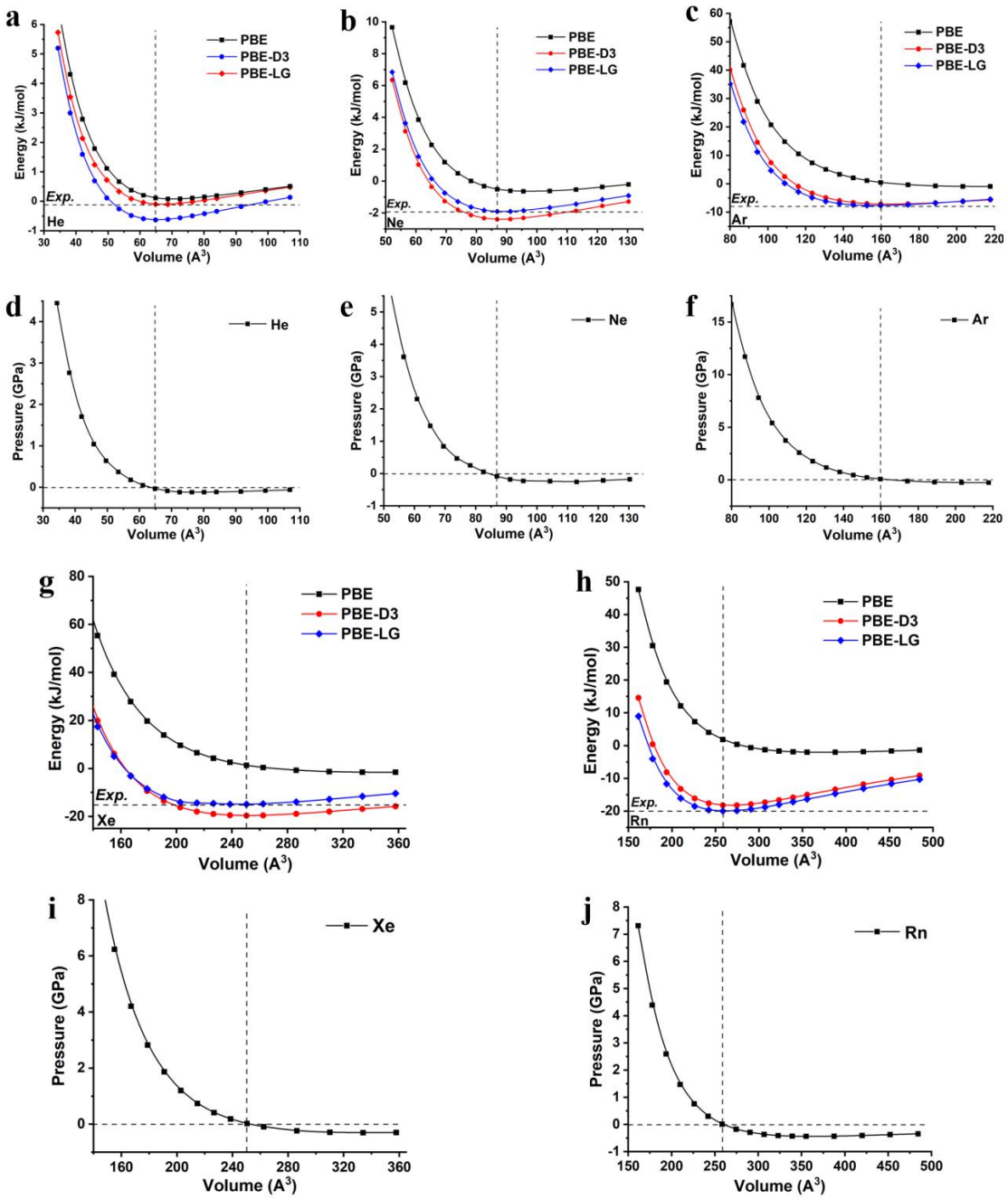

Figure S2. The equation of states (EOS) for (a, d) He, (b, e) Ne, (c, f) Ar, (g, i) Xe and (h, j) Rn using different methods. We got the LG parameters for noble gases by fitting the experimental heat of vaporization in EOS.

Table S1. The LG parameters for Carbon and Hydrogen used in this work.

Element	C_{6LG} / eV	R_{vdWLG} / Å
C	41.6545	3.6258
H	3.0924	2.7172

Table S2. The QM energy, ZPE, and delta enthalpy for benzene adsorbed on Pt (111) surface.

	QM energy / eV	ZPE / eV	delta enthalpy / eV (T=300 K)
Pt111-benzene	-297.219	2.879	0.652
Pt111 surface	-219.101	0.201	0.517
Benzene (ML)	-76.491	2.738	0.147
Benzene (molecule)	/	2.736	0.146

Table S3. The predicted adsorption energies of six hydrocarbons on metal surface using PBE-D3(BJ) (abbr. as D3) and PBE-LG (abbr. as LG), respectively. The energy unit here is kJ/mol.

	Ni(111) surface		Cu(111) surface		Ag(111) surface		Au(111) surface	
	D3	LG	D3	LG	D3	LG	D3	LG
CH_4	-20.16	-8.39	-20.14	-18.89	-16.73	-9.00	-17.23	-8.01
C_2H_6	-46.95	-27.70	-43.59	-32.15	-53.32	-34.18	-55.66	-37.88
C_3H_8	-37.71	-9.03	-44.21	-34.50	-50.89	-48.06	-57.94	-35.16
C_4H_{10}	-65.91	-40.08	-49.34	-32.99	-38.78	-24.84	-55.41	-12.09
C_6H_{10}	-119.62	-88.75	-87.35	-38.58	-114.40	-13.45	-91.80	-130.58
$C_{10}H_8$	-269.32	-227.03	-147.58	-120.22	-117.24	-58.86	-120.68	-109.03

5. Fitting for Ar dimer

First, *using the bulk-fitted parameters (PBE-LG) to predict the potential energy curves of Ar dimer*. The simulation results show that PBE-LG is much better than PBE in describing Ar dimer. For example, PBE-LG can well produce the optimal distance. Nevertheless, PBE-LG underestimate the binding energy by ~20% compared with the results from CCSD(T). This underestimation is consistent with the three-body repulsion.

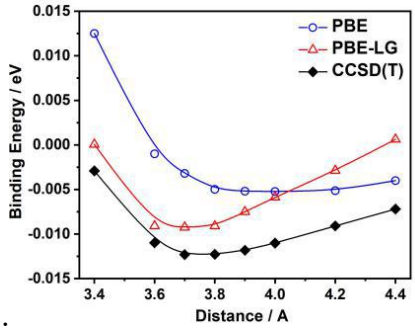

Figure S3. The potential energy curves for Ar dimers from PBE, PBE-LG and CCSD(T).

Second, *using the potential energy curves of Ar dimer to fit the parameters and use the new parameter to predict the bulk properties*. We fitted the parameters from the dimer calculations according to CCSD(T), resulting in the new parameter set of PBE-LG-2body. Compared with experimental results, the PBE-LG-2body significantly overestimate the cohesive energy. Again, this overestimation is consistent with the three-body repulsion.

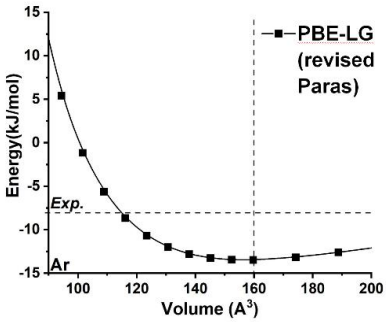

Figure S4. The equation of states curve for Ar using revised LG parameters, the black dashed line is referred to experimental heat of vapor.

References

1. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab initio Total-Energy Calculations Using a Plane-wave Basis Set. *Phys. Rev. B Condens. Matter* **1996**, *54*, 11169-11186.

2. Kresse, G.; Furthmüller, J. Efficiency of Ab-initio Total Energy Calculations for Metals and Semiconductors Using a Plane-wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15-50.

3. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

4. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 19.

5. Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456-1465.

6. Liu Y.; Goddard, W. A. First-Principles-Based Dispersion Augmented Density Functional Theory: From Molecules to Crystals. *J. Phys. Chem. Lett.* **2010**, *1*, 2550-2555.

7. Kim, H.; Choi, J.-M.; Goddard, W. A. Universal Correction of Density Functional Theory to Include London Dispersion. *J. Phys. Chem. Lett.* **2012**, *3*, 360-363.

8. Larsen, A. H.; Mortensen, J. J.; Blomqvist, Jakob.; *et. al.* The Atomic Simulation Environment-a Python Library for Working with Atoms. *J. Phys.: Condens. Matter* **2017**, *29*, 273002.

9. Carey, S. J.; Zhao, W.; Campbell, C. T. Energetics of Adsorbed Benzene on Ni(111) and Pt(111) by Calorimetry. *Surf. Sci.* **2018**, *676*, 9-16.